Spectroscopic and thermal properties of PU/PVC doped with multi walled carbon nanotube

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ABSTRACT

Nanocomposites based on (PU/PVC) polyurethane (PU) and poly (vinyl chloride) (PVC) loaded with low contents of multi walled carbon nanotubes (MWCNTs) were prepared using solution casting technique. The composition and structure of blend and nanocomposites were characterized by Fourier transform infrared spectroscopy (FTIR), Ultraviolet-visible spectroscopy (UV-Vis.) and Thermogravemetric (TGA). The spectroscopic study indicated that a strong interfacial interaction was developed between carbon nanotube (CNT) and the polymer matrix in the nanocomposites and optical energy gap direct and indirect decrease with increasing of MWCNTs. Thermal stability was studied by Thermogravimetric analysis (TGA)indicated that the behavior of thermal stability were enhanced after addition of MWCNTs into polymer blend and activation energy calculated by two method and decrease with increase of MWCNTs concentration . All results data showed well dispersed of MWCNTs in polymer matrix at all weight percentages.

Keywords: Nanocomposites; UV-Vis.; FT-IR; Thermal stability.

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INTRODUCTION

Polyurethane (PU) has attracted an outstanding amount of attention due to different applications for example thermoplastic, , biomedical devices, textiles [1]. The structure molecular of PU can be easily tailored to meet particular property requirements.

Poly vinyl chloride (PVC) is used in wide applications due to their well [2].It has PVC good properties like chemical resistance, not absorption of moisture water, high mechanical strength and self-extinguishing flame characteristics. Poly vinyl chloride is processed by itself, so it requires incorporation of different additives, because it's little thermal stability.

Blending of PU with other polymers has been of a considerable interest in literatures, for example poly (tetramethyleneadipate), polycaprolactone, polypropylene glycol-based PU[3,4]. However, few studies described blends of PU with PVC. Due to interaction between hydrogen bonds in both PU and PVC [5]. Adding PVC to PU is expand the characteristics of the blend to give compatibility of the blends and better mechanical property. By well dispersion of the nanoparticles or tubes of nanocarbon in a polymeric matrices, enhancement and performance of nanocomposites may be can be obtained to case-by-case applications [6].

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Carbon nanotubes (CNTs) incorporated into the polymeric matrices is attractive method to combine the optical, electronic and mechanical properties for individual CNTs with advantages of the polymer[7,8]. CNTs have attention of researchers and scientists because of their novel new west properties. Carbon nanotubes have been found to display excellent mechanical, electronic, and thermal properties [9]. In view of these properties, in addition nanometer scales and high aspect ratio, they are viewed as a perfect reinforcement for high strength nanocomposites. Farther more, carbon nanotubes are strongly influenced by Vander Waal's forces, it give more   information about aggregation, thus making their dispersion in polymers hard. To create novel composites, it is important to give well dispersed carbon nanotubes in matrix. Different methods have been advanced for the preparation of carbon nanotubes-polymers: electrospinning, mixing of melt, casting of solution, in situ polymerization, and surfactant-assisted processing of carbon nanotubes-polymers [10] . Carbon nanotubes have been utilized broadly as loaded on polymers to create mechanically stiffer materials and electrically conducting at low filler concentrations[11,12].The composites frequently exhibit further remarkable enhancements in physical properties and electromechanical [13]. The improved properties of these composites are primarily attributed to the Nano-scale dimension of carbon nanotube, its structure of   tubular graphitic and good electronic, thermal and mechanical properties [14].The purpose of the present study was the synthesis and characterization of PU/PVC doped with multi-wall CNTs (MWCNTs).

MATERIALS AND METHODS

Polyurethane (PU) (average molecular weight of 330600)Cargill-Dow, South Korea. High molecular weight polyvinyl chloride (PVC) supplied by (Fluka).Tetra hydro furan (THF)was obtained from Duksan chemicals (Korea) Purified functionalized multi-walled carbon nanotubes (MWCNTs-COOH) was supplied from NTX10, Nanothinx, Greece. MWCNTs have a diameter of 6–18 nm and length ≥20 µm (purity of 88%).

PU/PVC (75:25) Wt. % blend composite was dissolved in Tetrahydrofuran (THF) as a solvent $40^{o}C$ with continuous stirring until 24h for complete dissolution to form a homogeneous solution. The obtained solution of the blend was then cooled to room temperature for about 2 h to remove any bubbles. The pure MWCNT functionalized was mixed separately with the above solution under continuous stirring and occasional shaking in an ultrasonic for the appropriate dispersion of these nano materials inside the THF solution of polymer blend with different concentration of MWCNT (0.01, 0.02, 0.04, and 0.06 Wt. %) help to give a well dispersion of multi-walled carbon nanotube (MCNT). After that, the films of the (PU/PVC) – MWCNT were prepared on the glass plates using a solvent casting technique. The nanocomposites solution was put in an oven at room temperature to evaporate the solvent for about 72 hour.

Fourier transform-infrared spectra of the prepared films were examined using single beam light FTIR spectrometer (Nicolet *iS*10, USA) at room temperature range of spectral from about 4000-400 cm^{-1}.Ultra violet-visible absorption spectra measured in wavelength region of 200-900 nm using UNiCAM UV-Vis. Spectrometer, England to examine the changes in structures of the samples. Shimadzu Thermogravimetric -45H was utilized for TGA of films. A little amount of the film was taken to the measurement then the sample heated at room temperature in to 550 °C at rate of 10 °C min^{-1} in nitrogen atmosphere on platinum cell.

RESULTS AND DISCUSSION

3.1. Fourier Transform Infrared analysis (FT-IR)
Pure Multi wall carbon nanotubes as shown Fig. 1.a comprises of functional groups and the band centered around 3437 cm^{-1} ascribed to the OH stretching group which may be attributed to oscillation of carboxyl groups (O=C–OH and C–OH). The peak at 2922 cm^{-1} is refer to asymmetric stretching of CH_2, and at 2855 is attributed to symmetric stretching of CH_2. The absorption peak at 1735 cm^{-1} is corresponding to C=O stretching of COOH. The peak at 1630 cm^{-1} can be associated with the stretching of the CNTs backbone and peak at 1579 cm^{-1}is C=C, vibration bands at 1420 cm^{-1} and 1171 cm^{-1} are associated with O–H bending and C–O. It is generally assumed that these groups are located at defect locales on sidewall surface [15–17].

FT-IR spectra of the (PU/PVC) blend and its nanocomposites are shown in Fig.1.b It was clearly seen that the OH peak intensity at 3437 cm^{-1}, which shows peak in the MWCNTs, vanishes with the addition of multi walled carbon nanotubes in blend signified that multi walled carbon nanotubes were successfully covalently encapsulated by two layers of polymer. Polymer blend showed characteristic broad IR absorption bands at 3342 cm^{-1}, which is

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corroborated to -NH stretching bands of polyurethane (PU) [18]. Peaks at 2955 cm^{-1} attributed to (–CH asymmetric stretching), along with a shoulder at low wavenumber 2860 cm^{-1} (–CH symmetric stretching). The absorption band at 1702 assigned for hydrogen bonded C=O and 1729 cm^{-1} for free C=O. This split of C=O peak observed in Fig. 1.b may be because presence of inter-hydrogen bonding in polymer matrix. 1620 cm^{-1} –NH bending vibration, 1530 cm^{-1} C–C stretching. The absorption peaks at 1460 cm^{-1}, 1225 cm^{-1} and 1425 cm^{-1} corresponds to the alkane C-H bending, C-N stretching and CH_3 stretching of the blend. 1166 cm^{-1} C–O stretching of urethane groups and 837 cm^{-1} (C–Cl stretching). New peaks appear for some absorptions at 1415 cm^{-1} and 1171 attributed to of the MWCNT, 1230 cm^{-1} and 1315 cm^{-1} nearly disappear with increase concentration of CNT. This clearly showed that the chemical interaction between the MWCNT and polymer blend in the nanocomposites. All these changes in the FTIR spectra indicated interaction of polymer blends with MWCNT.

3.2 Optical properties
Ultraviolet–visible (UV-Vis.) spectroscopy corresponds to electronic excitations between the energy levels related to the molecular orbital of the system. All films of UV-Vis. spectra are recorded at room temperature in the range of 190-600 nm as shown in Fig. 2. Pure polymer blend and samples that filled with various concentration of MWCNT content nanocomposites exhibit absorbance in the ultra-violet range (200-380 nm).The absorption band at about 200 nm in pure blend was assigned to n→π* transitions and absorption band at 290 nm was assigned to π→π* transition. However, the observed spectra are characterized by the main absorption edge for all curves at about 290 nm which shifted toward longer wavelengths by about 20 nm with increasing MWCNT concentrations. These shifts in the bands indicate interactions between polymer blend chains with the nanotube surface[19].

The optical energy gap (E_g) for direct and indirect transitions can be determined by these equations:

$$(\alpha h\nu) = \beta_0 (h\nu)^r \qquad\qquad for\ h\nu > E_g \qquad\qquad\qquad\qquad (1)$$
$$(\alpha h\nu) = 0 \qquad\qquad\qquad for\ h\nu < E_g \qquad\qquad\qquad\qquad (2)$$

where E_g is the optical energy gap, β_o is a constant and r is the number which characterizes the optical absorption processes. It's that can take values r = 1/2: indirect- allowed transition, r=1: nonmetallic materials and 3/2: direct forbidden transition. r = 2 : direct- allowed transition, r= 3 : indirect forbidden transition [20].

Figure 3(a) show plot of the $(\alpha h\nu)^2$ as a function of photon energy (hν) and can be use equation (1) to calculate its direct optical energy gap and Fig. 3(b) show plot of the $(\alpha h\nu)^{1/2}$ as a function of photon energy (hν) and can be used to calculate its indirect optical energy gap; the resulting values are showed in Table (1). It is clear from Figures and the Table 1 that the indirect and direct band gap values showed a decrease with increasing MWCNT content. This decrease can be ascribed to the formation of defects in polymers and an increase in the degree of disorder in the samples. These defects create localized states in optical band gap. These overlaps are in charge for reduction energy band gap when concentration MWCNT increased in polymers [21].

3.3. Thermogravimetric analysis (TGA)
TGA is used to study thermal decomposition, mass change, and thermal stability of composite material[22]. Fig.7 shows the TGA curves pure blend with nanocomposites were heated from 35°C to 650 °C at 10 °C/min inside a nitrogen atmosphere. Based on the temperature change, the physical state of the nanocomposites undergoes changes coming from a glass transition into a high-elastic and viscous-flow state stepwise[23].Three major weight-loss were observed in every case. The initial weight-loss was observed at lower temperature may be observed a primary weight-loss for specimens that could be due to the the remainder solvent evolution, and the second weight loss in the range about 220 – 350 °C, for pure blend and nanocomposites, corresponding to the loss of HCl from PVC and loss of CO_2 from PU[24]and may be due to degradation of large polymer chains into small fragments. From 360 to 450 °C, this weight loss can be due to burning of organic phase and the thermal dehydration of inorganic particles [25]. Compared to pure blend, with nanocomposite showed higher stability, probably attributed to the combined effect of the excellent thermal stability of CNTs and their strong interfacial interactions with the polymer matrix and possible that the formation of compact char of carbon nanotubes and polymer matrix during the thermal degradation is beneficial to the improvement of thermal stability of the composites. It is very important to indicate the extent of interaction between MWNTs and polymer blend with higher dispersion could lead to an increased thermal stability with the composite system is compatible the results.

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Determination of the activation energy
Moreover, the thermodynamics activation parameters of the main decomposition process in the second degradation region of the present samples can be calculated using two different methods:

3.3. i -Coats - Redfern method

Coats - Redfern method is a typical integral method and can be represented in the following form[26]:

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = \log\frac{R}{\Delta E_a}\left[1 - \frac{2RT}{E_a}\right] - 0.434\frac{E_a}{RT} \tag{3}$$

Where, T is absolutely the temperature in Kelvin, Ea is the activation energy in J/mol, R may be the universal gas constant (8.3136 J/mol K), and also the fraction of conversion (α) for a weight-loss.

By plotting the dependence of $-\log\left[\dfrac{-\log(1-\alpha)}{T^2}\right]$ versus $\dfrac{1000}{T}$ for each sample, we obtained straight lines. Then,

the obvious activation energy are determined from slopes of these straight lines using:
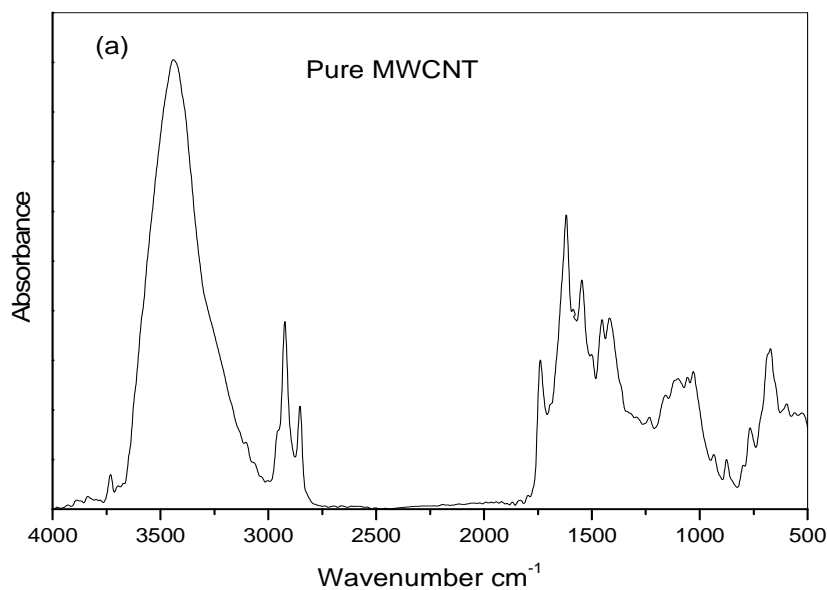
$E_a = 2.303R \times \text{slope}$ (4)

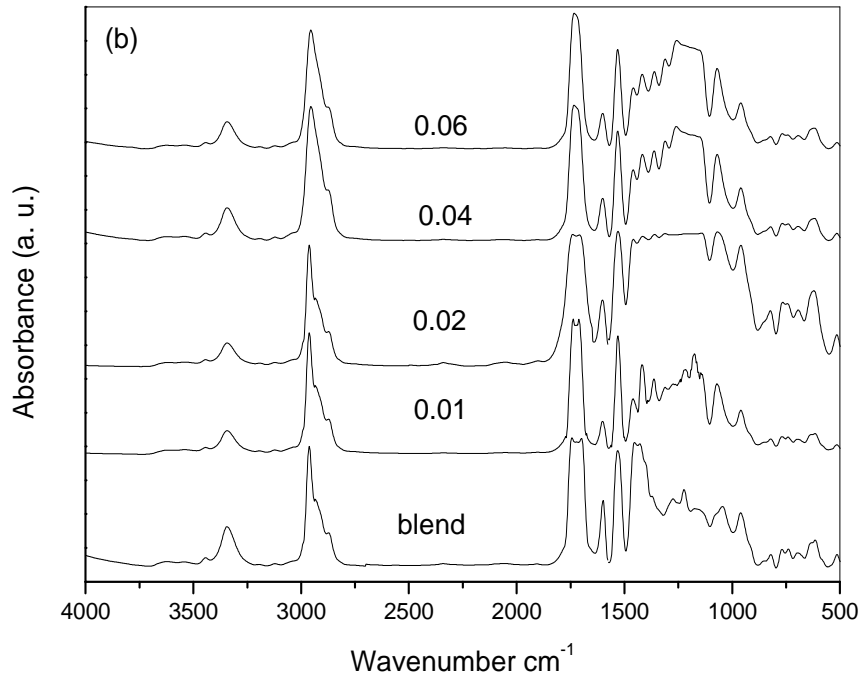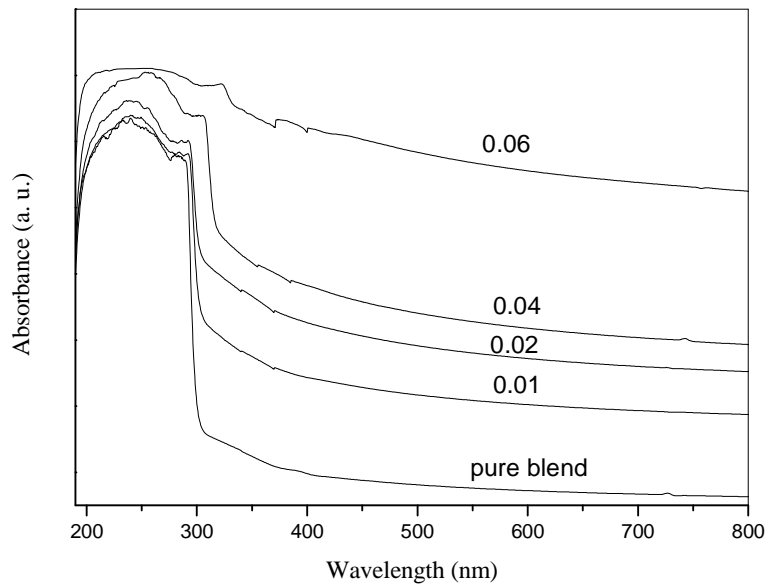**Fig. 1: FTIR spectra of (a) pure MWCNT (b) (PU/PVC) with different concentrations of MWCNT**

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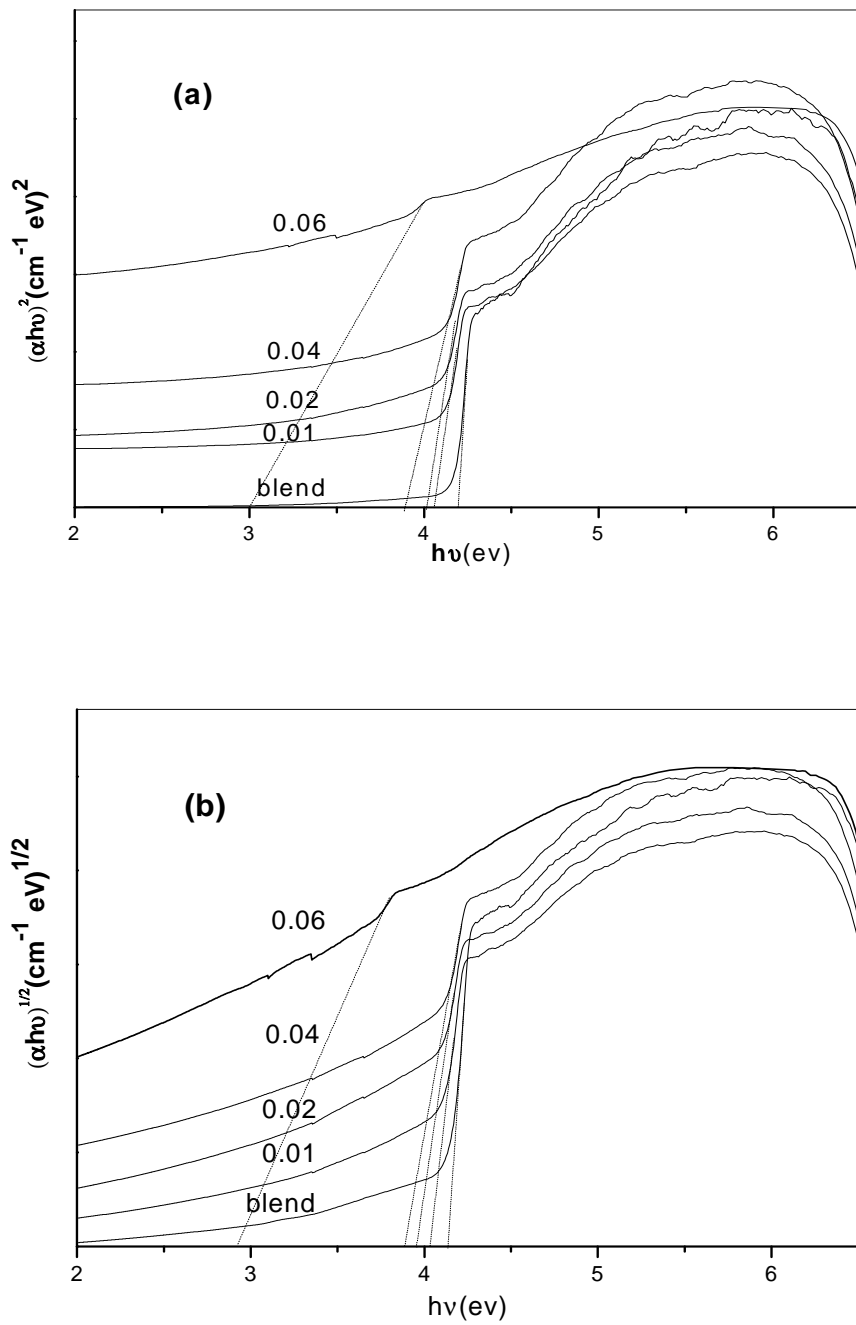**Fig. 2: UV. Vis. Spectra of (PU/PVC) with different concentrations of MWCNT**

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Fig 4: The relation between (a) αhν^2 (b) αhν$^{1/2}$ with hν at different concentrations of MCWNT
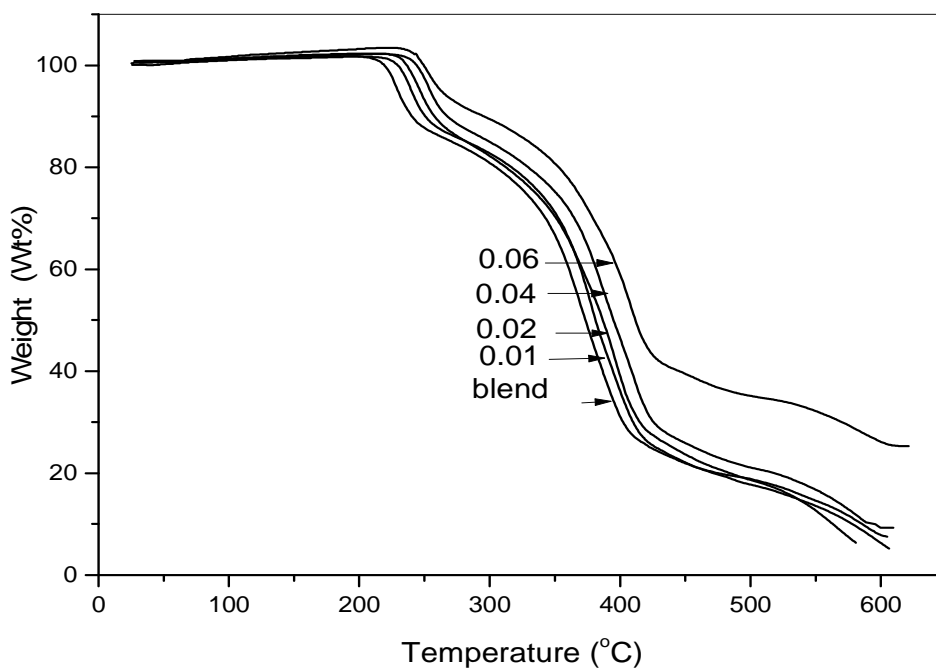
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Fig.3: TGA thermograms of (PU/PVC) with different concentrations of MWCNT

Table (1) the values direct, indirect band gap of optical energy gap and percentage crystallinity with different concentrations of MWCNT

Sample (PU/PVC) with MWCNT (Wt. %)	E_{gi} (eV) Indirect	E_{gd} (eV) direct
0.00	4.11	4.23
0.01	4.01	4.07
0.02	3.95	4.01
0.04	3.85	3.89
0.06	2.91	3.01

Table (2) the values of activation energy of (PU/PVC) with different concentrations of MWCNT

(PU/PVC) MWCNT (Wt. %)	Coats – Redfern method (KJ/mol)	Broido method (KJ/mol)
0.00	250.09	237.125
0.01	228.52	227.25
0.02	218.94	212.80
0.04	213.05	207.71
0.06	211.89	197.71

3.3. ii. Broido method
Broido introduce a model to evaluate the activation energy associated with second stage of decomposition using equation[27]:

$$\ln\left[\ln\left(\frac{1}{Y}\right)\right] = \left(\frac{E_a}{R}\right)\frac{1}{T} + C \tag{5}$$

Y is given by $Y = \dfrac{W_t - W_\infty}{W_i - W_\infty}$ (6)

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where, Y is the fraction of the number of initial molecules not yet decomposed; Wt- the weight at any time t; W∞- the weight at infinite time (= zero) and Wi- the initial weight. A plot of ln [ln (1/Y)] vs. 1/T gives an excellent approximation to a straight line. The slope is related to the activation energy. Values of the apparent activation energy (E_a) of the samples by two methods are listed in Table (2).

From the table, calculated of the activation energy decreases with increasing of CNTs contents indicates that CNTs intensively affect the polymer and agreement with results of optical energy gap of UV-Vis.

CONCLUSION

FTIR of the nanocomposites, shows shift and disappear of some bands, with the increase in MWCNTs weight percentage in the polymer. It's indicates a good physical entanglement between the constituents and clearly the interaction between the MWCNT and composites. UV-Vis. show shift of the peaks towards longer wavelength and the values energies gap were decreased with increasing MWCNT due to interaction between nanocomposites. TGA analysis indicated that the use of MWCNTs significantly enhancement the thermal stability induced by high thermal conductivity of MWCNTs. which suggested the functionalized MWNT substantially affected both amorphous and crystalline structure in the polymer matrices. It's clear the activation energy calculated from TGA decreasing with increasing of MWCNTs. The homogeneous dispersion of MWNTs through the polymer matrix at reduced MWNT loading and existence of strong interfacial adhesion between MWNTs and polymer matrices lead to the significant enhancement of overall material properties of the (PU/PVC)-MWNT nanocomposites. From these results, the PU/PVC-MWCNT nanocomposites.

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